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(54) **Water soluble ammonium siloxane compositions and their use as fiber treatment agents**

(57) The present invention relates to a water soluble ammonium siloxane composition comprising (A) an aminosiloxane solution comprising a mixture of (i) a triorganosilyl-endblocked aminofunctional siloxane, (ii) an aminofunctional siloxane which it triorganosiloxy-endblocked at one end and hydroxy-endblocked at the other end, and (iii) a hydroxy-endblocked aminofunctional siloxane, (B) a cyclic aminofunctional siloxane, and (C) a polydimethylcyclosiloxane where the aminofunctional group is selected from

$$-R^3-\overset{+}{N}HR^5-R^4-\overset{+}{N}H_2R^5\cdot 2A^-,\quad -R^3-\overset{+}{N}H_2-R^4-\overset{+}{N}HR^6\cdot A^-,$$

$$-R^3-NR^6-R^4-\overset{+}{N}H_3\cdot A^-,\quad -R^3-\overset{+}{N}H_2R^5\cdot A^-,$$

where R^3 is a divalent hydrocarbon radical, R^4 is a divalent hydrocarbon radical, R^5 is hydrogen, alkyl, aryl or arylalkyl, R^6 is a -C(O)R^7 group where R^7 is a monovalent hydrocarbon group or aryl and A^- is a halide anion, carboxylate anion or inorganic oxoanion. This invention further relates to a method of making the water soluble ammonium siloxane composition and to a method of treating a substrate with the water soluble ammonium siloxane composition.

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Description

U.S. Patent No. 4,891,166 discloses diquaternary polysiloxanes whose quaternary nitrogen groups are terminally linked to the polysiloxane molecule and their use in cosmetic preparations, especially in preparations for the care of hair. U.S. Patent No. 4,895,964 discloses a process for the manufacture of quaternary ammonium pendant siloxane copolymers by the reaction of epoxy pendant siloxane copolymers with a tertiary amine acid salt using a catalytic amount of a free tertiary amine as the catalyst. U.S. Patent No. 5,041,590 discloses a quaternary ammonium functional siloxane compound having the formula $[(R_3SiO)_2\text{-}SiR\text{-}(CH_2)_a]_bN^+R'_{4-b}X^-$ where R is an alkyl radical having one to six carbon atoms, R' is an alkyl or aryl radical having one to eight carbon atoms, X is a chloride, bromide, iodide, nitrate or RSO_4^-, a is an integer having a value from 1 to 10 and b is an integer having a value of 2 or 3. It is further disclosed that these siloxane compounds are useful in reducing the surface tension of an aqueous solution. U.S. Patent No. 5,235,082 discloses diquaternary ammonium functional siloxanes which have a variable amount of hydrophobicity at the center of the molecule which makes them useful in the field of fabric softening and fabric conditioning. U.S. Patent No. 5,364,633 discloses a method of entrapping a water-soluble substance in vesicles formed from a siloxane surfactant, where suitable siloxane surfactants include organosilicon compounds having the formula $RMe_2SiO(Me_2SiO)_a(MeRSiO)_bSiMe_2R$, $Me_3SiO(Me_2SiO)_a(MeRSiO)_bSiMe_3$ or $Me_3SiO(MeRSiO)SiMe_3$ where R can be a $\text{-}(CH_2)_xN^+R_3"A^-$, R" is an alkyl radical having from 1 to 6 carbon atoms, a benzyl radical, a phenyl radical or the radical $\text{-}CH_2CH_2OH$, A^- is chloride, bromide, iodide, cyanide, a methyl sulfate radical, a salicylate radical or a dodecylsulfate radical, a has a value of 0 to 200 and b has a value of 0 to 50 with the proviso that both a and b cannot both be zero. U.S. Patent No. 5,098,979 discloses silicone polymers which contain a quaternary nitrogen pendant group, where in one embodiment the quaternary nitrogen group has an alkylamido functionality and in a second embodiment it contains an imidazoline derived functionality and that these polymers are useful in softening hair, textile fibers and conditioning skin.

Other low molecular weight aminofunctional siloxanes are known to be water-soluble. U.S. Patent Nos. 5,087,715 and 5,104,576 discloses alkanolaminofunctional siloxanes which are useful in altering the surface activity of water, the siloxanes having the formula $R^1_3SiO(R^1MSiO)_ySiR^1_3$ or $R^1_3SiO(R^1_2SiO)_x(R^1MSiO)_ySiR^1_3$ where x is an integer from 1 to 100, y is an integer from 1 to 10, R^1 is a lower alkyl group and M is an alkanolamino group having the formula $\text{-}(CH_2)_aN(R^2)\text{-}(CH_2)_bOR^3$ or $\text{-}(CH_2)_aN\text{+}(R^2)(R^4)\text{-}(CH_2)_bOR^3Z^-$ where a is an integer from 1 to 10, b is an integer from 1 to 10, R^2 is hydrogen, a C_1 to C_{18} alkyl group, a C_6 to C_{18} aryl group, $\text{-}CH_2\text{-}C_6H_5$ or a C_5 to C_{18} cycloalkyl group, R^3 is hydrogen, a C_1 to C_{18} alkyl group, a C_6 to C_{18} aryl group, a C_5 to C_{18} cycloalkyl group, $\text{-}C(O)R^5$, $\text{-}C(O)NHR^6$, $\text{-}SO_3^-$, $\text{-}Si(CH_3)_3$ or $\text{-}P(O)(OCH_3)_2$, R^4 is hydrogen, a C_1 to C_{18} alkyl group, a C_6 to C_{18} aryl group, $\text{-}CH_2\text{-}C_6H_5$ or a C_5 to C_{18} cycloalkyl group, R^5 and R^6 are a C_1 to C_{18} alkyl group, a C_6 to C_{18} aryl group or a C_5 to C_{18} cycloalkyl group and Z is Cl, Br, I, NO_3, a C_1 to C_8 alkylsulfate group, $\text{-}CH_3COO^-$, BF_4^- or PF_6^-. U.S. Patent No. 5,026,489 discloses a fabric softening composition which includes an alkanolamino functional silicone compound having the formula $(R_3SiO)_2SiR\text{-}(CHR')_aN^+R'_bR"_{3-b}X^-$ where R is an alkyl radical having one to six carbon atoms, R' is hydrogen, alkyl and aryl radicals having one to eighteen carbon atoms, R" is (CHR')OH, X is a chloride, bromide, iodide, nitrate or RSO_4^-, a is an integer having a value from 1 to 10 and b is an integer having a value of 1 or 2.

Polymeric ammonium functional siloxanes have also been taught. U.S. Patent Nos. 4,472,566 and 4,597,964 discloses cationic polydiorganosiloxanes having the general formula $QMe_2SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2Q$ where Me denotes methyl and R is a radical having the formula $\text{-}C_mH_{2m}NHC_nH_{2n}N^+H_2CH_2C_6H_5Cl^-$ or $C_mH_{2m}N^+(CH_2C_6H_5Cl^-)HC_nH_{2n}N^+H_2CH_2C_6H_5Cl^-$ where m has a value of 2 to 5 inclusive and n has a value of 1 to 5 inclusive, Q is R, methyl or OH, x has a value of 5 to 200 and y has a value of 1 to 30. These siloxanes are useful for treating human hair, human skin and animal fur is also disclosed.

Reactive ammonium-functional siloxanes have also been disclosed in the art. U.S. Patent No. 3,355,424 discloses a process for the preparation of polyaminoalkyl-substituted organosiloxane copolymers and salts thereof and to the reaction products of said processes. U.S. Patent Nos. 3,544,498 and 3,576,779 discloses an organopolysiloxane copolymer which is prepared by the partial hydrolysis and condensation of a silanol-chainstopped polydimethylsiloxane having 5 siloxy units, an aminoalkyltrialkoxysilane and an aminoalkoxyalkyltrialkoxysilane. A second organopolysiloxane copolymer can be prepared by the partial hydrolysis and condensation of a silanol-chainstopped polydimethylsiloxane having 800 dimethylsiloxy units with an aminoalkoxyalkenyltrialkoxysilane is also disclosed. The first organopolysiloxane polymer can be converted to a partial amine salt by reaction with an aliphatic carboxylic acid, then mixed with the second organopolysiloxane. U.S. Patent No. 3,890,269 discloses a process for preparing aminofunctional organopolysiloxanes which comprises equilibrating a mixture containing an organopolysiloxane and an aminofunctional silane or siloxane in the presence of a catalyst. It is further disclosed that the aminofunctional groups present in the organopolysiloxanes which are prepared can be reacted with organic or inorganic acids to form the corresponding ammonium salts. U.S. Patent No. 5,110,891 teaches a polish formulation which contains a reactive amine functional silicone polymer.

Other water-insoluble ammonium siloxanes which result from the reaction of amino-siloxanes and organic carboxylic acids have been taught. U.S. Patent No. 5,115,049 discloses fatty carboxylic acid salts of organofunctional silicone

amines where the amino pendant functionality is present within the polymer.

Unreactive linear amino-siloxanes have also been described. U.S. Patent No. 2,947,771 discloses the production of endblocked organopolysiloxanes containing among other siloxane units, aminoalkylalkylsiloxane or aminoalkylaryl-siloxane units in which the amino group is linked to the silicon atoms through a polymethylene chain of at least three carbon atoms.

The present invention relates to water soluble ammonium siloxane compositions, a method of making water soluble ammonium siloxane compositions and the use of these compositions as fiber treatment agents.

The present invention produces novel linear silicone-unreactive water-soluble ammonium functional siloxane compositions.

This invention also produces water-soluble ammonium functional siloxane compositions which are useful as fiber treatment agents.

Ammonium functional siloxane compositions prepared by this invention which, when applied to fibers such as paper pulp or tissue, render the fibers soft and smooth to the touch.

Water-soluble ammonium functional siloxane compositions produced by this invention have at least 10 mole percent ammonium-methylsiloxane functionality.

The present invention relates, in a first embodiment, to a water soluble ammonium siloxane composition comprising (A) 0.01 to 90 weight percent of an aminosiloxane blend comprising a mixture of (i) an aminofunctional siloxane having its formula selected from (a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR^3$ and (b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_3$, and (ii) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$, and (iii) an aminofunctional siloxane having its formula selected fro
(a) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$, (B) 0.1 to 90 weight percent of a cyclic aminofunctional siloxane having the formula

$$\text{(i)} \qquad \boxed{(Me_2SiO)_{x'}(RR^1SiO)_{y'}} \ ,$$

and
(C) 0.1 to 10 weight percent of a compound having the formula:

$$\text{(i)} \qquad \boxed{(Me_2SiO)_n}$$

wherein Me denotes methyl, R is independently a monovalent hydrocarbon radical having from 1 to 6 carbon atoms or an aryl radical, R^1 is a group having its formula selected from $-R^3-NHR^5-R^4-NH_2R^5 \cdot 2A^-$, $-R^3-NH_2-R^4-NHR^6 \cdot A^-$, $-R^3-NR^6-R^4-NH_3-A^-$, $-R^3-NH_2R^5 \cdot A^-$ and wherein R^3 is a divalent hydrocarbon radical having at least 3 carbon atoms, R^4 is a divalent hydrocarbon radical having at least 2 carbon atoms, R^5 is selected from hydrogen, an alkyl radical having from 1 to 6 carbon atoms, an aryl radical and an arylalkyl radical, R^6 is a $-C(O)R^7$ group where R^7 is selected from a monovalent hydrocarbon group having from 1 to 20 carbon atoms and an aryl radical and A^- is an anion selected from halide anions, carboxylate anions and inorganic oxoanions, R^2 is independently selected from a monovalent hydrocarbon radical having from 2 to 6 carbon atoms and an aryl radical, x has a value of 10 to 10,000, y has a value of 1 to 8,000, z has a value of 1 to 250, x' has an average value of 1 to 8 and y' has an average value of 1 to 8 with the proviso that the value of x'+ y' is from 4 to 9, n has an average value of 4 to 9 and with the proviso that the value of y/x+y+z+2 is at least 0.1.

The monovalent hydrocarbon radicals of R are exemplified by alkyl radicals such as methyl, ethyl, propyl, pentyl or hexyl and the aryl radicals are exemplified by phenyl, tolyl or xylyl. R is preferably methyl or phenyl. The monovalent hydrocarbon radicals of R^2 are exemplified by ethyl, propyl, butyl, pentyl or hexyl and the aryl radicals are as defined above for R. Preferably, R^2 is independently selected from ethyl, propyl, butyl, hexyl, phenyl, tolyl and xylyl.

The divalent hydrocarbon radicals of R^3 are exemplified by groups such as alkylene groups including propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethylhexamethylene, oc-

tamethylene, $-CH_2(CH_3)CH-$, $-CH_2CH(CH_3)CH_2-$, $-(CH_2)_{18}-$ and cycloalkylene radicals such as cyclohexylene, arylene radicals such as phenylene, combinations of divalent hydrocarbon radicals such as benzylene ($-C_6H_4CH_2-$) and oxygen containing groups such as $-CH_2OCH_2-$, $-CH_2CH_2CH_2OCH_2-$, $-CH_2CH_2OCH_2CH_2-$, $-COOCH_2CH_2OOC-$, $-CH_2CH_2OCH(CH_3)CH_2-$ and $CH_2OCH_2CH_2OCH_2CH_2-$. Preferably R^3 is selected from the group consisting of propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethylhexamethylene and octamethylene.

The divalent hydrocarbon radicals of R^4 are exemplified by ethylene or any of the divalent hydrocarbon radicals delineated for R^3 hereinabove. Preferably R^4 is selected from ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene and octamethylene.

The alkyl radicals and aryl radicals of R^5 are as delineated for R hereinabove. The arylalkyl radicals of R^5 are exemplified by benzyl and 2-phenylethyl. It is preferred that R^5 is selected from the group consisting of hydrogen, methyl, phenyl and benzyl.

The group R^6 is a

$$-C(O)R^7(\overset{\overset{\displaystyle O}{\|}}{C}R^7)$$

group where R^7 is a monovalent hydrocarbon group having from 1 to 20 carbon atoms or an aryl radical. The monovalent hydrocarbon groups of R^7 are exemplified by methyl, ethyl, propyl, $-C_6H_5$ and a group having the formula $-(CH_2)_nCH_3$ where n has a value of 4 to 18.

The halide anions of A^- are exemplified by Cl^-, Br^-, I^- and F^-, the carboxylate anions of A^- are exemplified by CH_3COO^-, $HOCH_2COO^-$, $C_6H_5COO^-$, $HOC_6H_4COO^-$, $CH_3CH_2COO^-$, $CH_3CH_2CH_2COO^-$, $CH_3CH(OH)CH_2COO^-$, $CH_3(CH_2)_4COO^-$, $CH_3(CH_2)_3CH(OH)COO^-$, $CH_3(CH_2)_6COO^-$, $CH_3(CH_2)_8COO^-$, $HO(CH_2)_9COO^-$, $CH_3(CH_2)_{10}COO^-$, $HO(CH_2)_{11}COO^-$, $CH_3(CH_2)_{14}COO^-$, $HO(CH_2)_{15}COO^-$, $CH_3(CH_2)_{16}COO^-$, $CH_3(CH_2)_5CH(OH)(CH_2)_{10}COO^-$, $ClC_6H_4COO^-$ and the inorganic oxoanions are exemplified by ClO^-, ClO_3^-, ClO_2^-, ClO_4^-, $SO_4^=$, $PO_4^{\equiv}$, HCO_2^-, NO_3^-, $CO_3^=$ and HCO_3^-.

Preferably, (A)(i) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_3$, (A)(ii) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, (A) (iii) is an aminofunctional siloxane having the formula $HOMe_2SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$ and (B) is a cyclic aminofunctional siloxane having the average formula:

$$\left[(Me_2SiO)_x \cdot (MeR^1SiO)_y \cdot\right]$$

wherein R^1 is a group having its formula selected from:

$$-CH_2CH_2CH_2-\overset{+}{N}H_2-CH_2CH_2-\overset{+}{N}H_3 \cdot 2A^-,$$

$$-CH_2CH(CH_3)CH_2-\overset{+}{N}H_2-CH_2CH_2-\overset{+}{N}H_3 \cdot 2A^-,$$

$$-CH_2CH_2CH_2-\underset{\displaystyle CH_2C_6H_5}{\overset{+}{N}H}-CH_2CH_2-\underset{\displaystyle CH_2C_6H_5}{\overset{+}{N}H_2} \cdot 2A^-,$$

$$-CH_2CH(CH_3)CH_2-\overset{+}{N}H(CH_2C_6H_5)-CH_2CH_2-\overset{+}{N}H_2(CH_2C_6H_5)\cdot 2A^-,$$

$$-CH_2CH_2CH_2-\overset{+}{N}H_2-CH_2CH_2-NH(C(O)CH_3)\cdot A^-,\quad -CH_2CH(CH_3)CH_2-N(C(O)CH_3)-CH_2CH_2-\overset{+}{N}H_3\cdot A^-,$$

and $-CH_2CH_2CH_2-\overset{+}{N}H_3\cdot A^-$ wherein A^- is selected from CH_3COO^-, Cl^-, $HOCH_2COO^-$, $C_6H_5COO^-$ and $HOC_6H_4COO^-$ wherein x, y, x' and y' are as defined above.

It is also preferred that in the compositions of the invention, x has a value of 10 to 100, y has a value of 5 to 50, x' has a value of 2 to 3.5 and y' has a value of 0.5 to 2 with the proviso that the value of x'+ y' is 4.

The compositions of the present invention comprise 0.01 to 90 weight percent of component (A), 0.1 to 90 weight percent of component (B) and 0.1 to 10 weight percent of component (C) such that the combined weight percent of components (A)+(B)+(C) is 100 weight percent.

In a second embodiment, the present invention relates to a method of making a water soluble ammonium siloxane composition comprising mixing (I) a blend comprising (A) 0.01 to 90 weight percent of an aminosiloxane solution comprising a mixture of (i) an aminofunctional siloxane having its formula selected from

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_3$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_3$, and (ii) an aminofunctional siloxane having its formula selected from
(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$, and (iii) an aminofunctional siloxane having its formula selected from
(a) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$, (B) 0.1 to 90 weight percent of a cyclic aminofunctional siloxane having the average formula

$$\text{(i)}\qquad \left[(Me_2SiO)_{x'}(RR^1SiO)_{y'}\right],$$

and
(C) 0.1 to 10 weight percent of a compound having the formula:

$$\text{(i)}\qquad \left[(Me_2SiO)_n\right]$$

wherein Me denotes methyl, R is independently a monovalent hydrocarbon radical having from 1 to 6 carbon atoms or an aryl radical, R^1 is a group having its formula selected from $-R^3NH-R^4-NH_2$ and $-R^3-NH_2$ wherein R^3 is a divalent hydrocarbon radical having at least 3 carbon atoms, R^4 is a divalent hydrocarbon radical having at least 2 carbon atoms, R^2 is independently selected from monovalent hydrocarbon radical having from 2 to 6 carbon atoms and an aryl radical, x has a value of 10 to 10,000, y has a value of 1 to 8,000, z has a value of 1 to 250, x' has an average value of 1 to 8 and y' has an average value of 1 to 8 with the proviso that the value of x'+ y' is from 4 to 9, n has an average value of 4 to 9 and with the proviso that the value of y/x+y+z+2 is at least 0.1; (II) an acid compound; and (III) water.

In the above method, the monovalent hydrocarbon radicals and aryl radicals of R are as described hereinabove. Preferably, R is methyl or phenyl. The monovalent hydrocarbon radicals and aryl radicals of R^2 are as described here-

inabove. Preferably, R^2 is independently selected from the group consisting of ethyl, propyl, butyl hexyl, phenyl, tolyl and xylyl.

The divalent hydrocarbon radicals of R^3 are as described hereinabove. Preferably, R^3 is selected from the group consisting of propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene and octamethylene.

The divalent hydrocarbon radicals of R^4 are as described hereinabove. Preferably, R^4 is selected from the group consisting of ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene and octamethylene.

In this method of the invention, it is preferred that (A)(i) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_3$, (A) (ii) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, (A) (iii) is an aminofunctional siloxane having the formula $HOMe_2SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$ and (B) is a cyclic aminofunctional siloxane having the formula:

$$\left[(Me_2SiO)_{x'} (MeR^1SiO)_{y'} \right]$$

wherein R^1 is a group having its formula selected from $-CH_2CH_2CH_2-NH-CH_2CH_2-NH_2$, $-CH_2CH(CH_3)CH_2-NH-CH_2CH_2-NH_2$ and $-CH_2CH_2CH_2-NH_2$ wherein x, y, x' and y' are as defined above.

It is preferred in this method of the invention that x has a value of 10 to 100, y has a value of 5 to 50, x' has a value of 2 to 3.5 and y' has a value of 0.5 to 2 with the proviso that the value of x'+ y' is 4.

In the method of the present invention, there is present in component (I), 0.01 to 90 weight percent of component (A), 0.1 to 90 weight percent of component (B) and 0.1 to 10 weight percent of component (C) such that the combined weight percent of components (A)+(B)+(C) is 100 weight percent.

It is preferred for purposes of this invention that from 0.01 to 90 weight percent of Component (I) is used and it is highly preferred that from 0.1 to 90 weight percent of Component (I) be employed.

The acid compound of component (II) in this method of the invention can be an inorganic acid or an organic acid and can be a strong acid or a weak acid. Preferably the acid is a mineral acid or a carboxylic acid. The carboxylic acid can be for example, an aliphatic carboxylic acid exemplified by acetic acid and formic acid or an aromatic carboxylic acid exemplified by benzoic acid or salicylic acid. Acids suitable as component (II) include CH_3COOH (acetic acid), HCOOH (formic acid), $HOCH_2COOH$ (glycolic acid), C_6H_5COOH (benzoic acid), HOC_6H_4COOH (2-, 3- or 4- hydroxybenzoic acid), CH_3CH_2COOH (propionic acid), $CH_3CH_2CH_2COOH$ (butyric acid), $CH_3CH(OH)CH_2COOH$ (3- hydroxybutyric acid), $CH_3(CH_2)_4COOH$ (hexanoic acid), $CH_3(CH_2)_3CH(OH)COOH$ (2-hydroxyhexanoic acid), $CH_3(CH_2)_6COOH$ (octanoic acid), $CH_3(CH_2)_8COOH$ (decanoic acid), $HO(CH_2)_9COOH$ (10-hydroxydecanoic acid), $CH_3(CH_2)_{10}COOH$ (lauric acid), $HO(CH_2)_{11}COOH$ (12-hydroxydodecanoic acid), $CH_3(CH_2)_{14}COOH$ (palmitic acid), $HO(CH_2)_{15}COOH$ (16-hydroxyhexadecanoic acid), $CH_3(CH_2)_{16}COOH$ (stearic acid), $CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOH$ (12-hydroxystearic acid), $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (oleic acid), ClC_6H_4COOH (2-, 3- or 4-chlorobenzoic acid), HCl (hydrochloric acid), HBr (hydrobromic acid), HI (hydrogen iodide), HF (hydrogen fluoride), H_2CO_2 (formic acid), HNO_3 (nitric acid), H_3PO_4 (phosphoric acid), H_2CO_3 (carbonic acid), H_2SO_4 (sulfuric acid), $HClO_4$ (perchloric acid), $HClO_3$ (chloric acid), $HClO_2$ (chlorous acid) and HClO (hyprochloric acid).

It is preferred that from 0.01 to 50 weight percent of Component (II) is used and it is highly preferred that from 0.1 to 10 weight percent of Component (II) be employed.

Component (III) in this method of the invention is water. It is preferred for purposes of this invention that from 1 to 99.9 weight percent of Component (III) is used and it is highly preferred that from 10 to 99.9 weight percent of Component (III) be employed.

In the method of this invention, Component (I) is present at 0.01 to 90 weight percent, Component (II) is present at 0.01 to 50 weight percent and Component (III) is present at 1 to 99.9 weight percent such that the combined weight percent of components (I)+(II)+(III) is 100 weight percent.

The method of this invention can further comprise adding an acid anhydride during step (I). The acid anhydride is exemplified by $(CH_3CO)_2O$ (acetic anhydride), $(C_6H_5CO)_2O$ (benzoic anhydride), $CH_3CH_2COOCOCH_2CH_3$ (proprionic anhydride), $(CH_3CH_2CH_2CO)_2O$ (butyric anhydride), $(CH_3(CH_2)_4CO)_2O$ (hexanoic anhydride), $(CH_3(CH_2)_8CO)_2O$ (decanoic anhydride), $(CH_3(CH_2)_{10}CO)_2O$ (lauric anhydride), $(CH_3(CH_2)_{14}CO)_2O$ (palmitic anhydride), $(CH_3(CH_2)_{16}CO)_2O$ (stearic anhydride).

It is preferred that if an acid anhydride is employed, from 0.01 to 20 weight parts of acid anhydride is used and it is highly preferred from 0.01 to 10 weight parts of acid anhydride be employed per 100 weight parts of components (I)+(II)+(III).

The method of this invention can further comprise adding an aryl halide during step (I). The aryl halide is exemplified

by benzyl chloride, benzyl bromide, benzyl iodide, benzyl fluoride, phenyl chloride, phenyl bromide or phenyl fluoride.

It is preferred that if an aryl halide is employed, that from 0.01 to 10 weight parts of aryl halide is used and it is highly preferred that from 0.01 to 5 weight parts of aryl halide be employed per 100 weight parts of components (I)+(II)+(III).

In a third embodiment, the present invention relates to a method of treating a substrate, the method comprising the step of (I) applying to a substrate a water soluble ammonium siloxane composition wherein the water soluble ammonium siloxane composition comprises the water soluble ammonium siloxane composition described in the first embodiment of this invention hereinabove including preferred embodiments and amounts thereof.

The water soluble ammonium siloxane compositions of this invention may be applied to the substrate by employing any suitable application technique, such as by padding, spraying or from a bath. The compositions are applied neat (i.e. 100 wt% water soluble ammonium siloxane solution) or are further diluted in water prior to application to the substrate. The concentration of the treating solution will depend on the desired level of application of siloxane to the substrate and on the method of application employed, but it is believed that the most effective amount of the composition should be in the range such that the substrate picks up the silicone composition at 0.05% to 10% based on the weight of the substrate.

In this method, the substrate is preferably a fiber or fabric. The fibers, usually in the form of tow or knitted or woven fabrics, are immersed in a neat or a water diluted solution of the water soluble ammonium siloxane composition whereby the composition becomes selectively deposited on the fibers. The deposition of the ammonium siloxane composition on the fibers may also be expedited by increasing the temperatures of the bath with temperatures in the range of from 20 to 60°C. being generally preferred.

The compositions of this invention can be employed for the treatment of substrates such as animal fibers such as wool, cellulosic fibers such as cotton and synthetic fibers such as nylon, polyester and acrylic fibers or blends of these materials, such as polyester/cotton blends and may also be used in the treatment of leather, paper, paper pulp, tissues such as bath tissue or facial tissue and gypsum board. The fibers may be treated in any form, for example, as knitted and woven fabrics and as piece goods. They may also be treated as agglomerations of random fibers as in filling materials for pillows and the like such as fiberfil. The compositions of the invention are especially useful for treating paper pulp and bath or facial tissue.

In this embodiment of the invention, the method can further comprise heating the substrate after step (I). Thus, following the application of the water soluble ammonium siloxane composition to the substrate, the siloxane can then be cured. Curing is expedited by exposing the treated fibers to elevated temperatures, preferably from 50 to 200°C.

The water soluble ammonium siloxane composition of this invention should be used at 0.05 to 25 weight percent in the final bath for exhaust method applications and 5 gm/l to 80 gm/l in a padding method of application and 5 gm/l to 600 gm/l for a spraying application. The fibers or fabrics treated with the compositions of this invention have superior slickness, have no oily feeling and are soft to the touch.

Examples 1-10

The following compositions of the present invention were prepared by mixing an aminosiloxane solution described below, an acid and water into a container. This mixture was then agitated until the mixture was homogenous. In Examples 1 and 2, the acid and aminosiloxane solution were mixed first and this was then followed by the addition of water.

In Example 5, the solution was prepared by mixing 150.2 (g) of the aminosiloxane solution described below and 150.35 (g) of isopropyl alcohol in a 2000 ml flask. Next, with stirring, 41.80 (g) of benzyl chloride was added with a dropper and the resulting mixture was again stirred. The mixture was then heated to a temperature of 85°C. and then allowed to cool. After cooling, the solution was placed in an evaporating dish in the hood to remove most of the isopropyl alcohol. The remaining isopropyl alcohol was removed by heating the solution in a beaker. The resulting polymer was then mixed with water and acid. The Example 9 solution was prepared according to the same procedure as was used for Example 5, except that 150.33 (g) of aminosiloxane solution, 153.03 of isopropyl alcohol and 59.73 (g) of benzyl chloride were used. The amount of aminosiloxane solution, acid and water for all the examples is in Table 1.

Each of the aminosiloxane solutions contained (i) a mixture of an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$, an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, an aminofunctional siloxane having the average formula $HOMe_2SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, (ii) a cyclic aminofunctional siloxane having the average formula

$$\left[(Me_2SiO)_{x'}(MeRSiO)_{y'}\right] ,$$

and
(iii) a cyclosiloxane having the average formula

$$\boxed{(Me_2SiO)_n}$$

where R is a group having the formula $-CH_2CR^1HCH_2-NH-CH_2CH_2-NH_2$ where R^1 is methyl or a hydrogen atom, the value of x'+ y' is from 4 to 9 and n has an average value of 4 to 9. The amount of each component in each solution was as follows: Example 1 contained 79 weight percent of (i), 13 weight percent of (ii) and 8 weight percent of (iii), Example 2 contained 78 weight percent of (i), 15 weight percent of (ii) and 7 weight percent of (iii), Examples 3-5, contained 73 weight percent of (i), 20 weight percent of (ii) and 7 weight percent of (iii) and Examples 6-9 contained 44 weight percent of (i), 51 weight percent of (ii), 5 weight percent of (iii) and Example 10 contained 45 weight percent of (i), 52 weight percent of (ii), 3 weight percent of (iii). The value of x and y, the acid employed in the particular example and the identity of R^1 are delineated in Table 1 hereinbelow.

Table 1

Ex	x	y	R^1	Acid	Wt% Siloxane	Wt% Acid	Wt% Water
1	47	8	-H	CH_3COOH	0.7918	0.2068	99.0014
2	44	9	$-CH_3$	CH_3COOH	2.3971	0.5991	97.0038
3	36	10	-H	CH_3COOH	13.0259	3.2994	83.6747
4	35	10	-H	$HOCH_2COOH$	13.3802	4.1462	82.4736
5	36	10	-H	CH_3COOH	1.6248	0.3847	97.9905
6	23	13	-H	CH_3COOH	59.0998	20.4340	20.4662
7	23	13	$-CH_3$	CH_3COOH	58.6525	21.3436	20.0039
8	23	13	-H	$HOCH_2COOH$	41.2080	17.3892	41.4028
9	20	13	$-CH_3$	CH_3COOH	74.1808	15.6196	10.1996
10	11	15	$-CH_3$	CH_3COOH	60.7800	29.4800	9.7400

The resulting solutions (examples) contained components (i), (ii) and (iii) in the amounts delineated above however, R was a group having the formula $-CH_2CR^1HCH_2-NHR^2-CH_2CH_2-NH_2R^2\cdot 2A^-$ where R^1 is methyl or a hydrogen atom and R^2 is a hydrogen atom or a $-CH_2C_6H_5$ group. The value of x, y, x' and y' for the solutions remained the same. The identity of A, the identity of R^1, the identity of R^2, the mole percent of MeRSiO and the neutralized polymer solubility (weight percent aminofunctional siloxane in H_2O) are delineated in Table 2 hereinbelow. The mole percent of MeRSiO was determined using the following formula: Mole percent MeRSiO = 100(y/x+y+2). The samples were visually observed after completion of the mixing of the above components. If the sample was clear, this indicated that the polymer was water soluble. Examples 1-10 were all determined to be water soluble.

Table 2

Example	R^1	R^2	A	MeRSiO Mole (%)	Polymer Solubility (wt% in H_2O)
1	-H	-H	CH_3COO^-	14	1
2	$-CH_3$	-H	CH_3COO^-	16	3
3	-H	-H	CH_3COO^-	20	18
4	-H	-H	$HOCH_2COO^-$	20	17
5	-H	$-CH_2C_6H_5$	Cl^-	20	2
6	-H	-H	CH_3COO^-	32	80
7	$-CH_3$	-H	CH_3COO^-	32	80
8	-H	-H	$HOCH_2COO^-$	32	58
9	$-CH_3$	$-CH_2C_6H_5$	Cl^-	32	90
10	$-CH_3$	-H	CH_3COO^-	50	90

Comparison Examples 1-8

The following compounds were prepared by mixing an aminofunctional siloxane polymer described below, an acid and water into a container. In Comparison Example 3, the solution was prepared by mixing 350.10 (g) of the aminofunctional siloxane polymer described below and 150.05 (g) of isopropyl alcohol in a 2000 ml flask. Next, with stirring, 11.70 (g) of benzyl chloride was added with a dropper and the resulting mixture was again stirred. The mixture was then heated to a temperature of 85°C. and then allowed to cool. After cooling, the solution was placed in an evaporating dish in the hood to remove most of the isopropyl alcohol. The remaining isopropyl alcohol was removed by heating the solution in a beaker. The resulting solution was then mixed with water and acid. Examples 7 and 8 were prepared according to the procedure of Example 3, except that 150.01 (g) of aminosiloxane, 151.51 (g) of isopropyl alcohol and 18.78 (g) of benzyl chloride were used. The amount of aminofunctional siloxane polymer, acid and water for Comparison Examples 1-8 is delineated in Table 3 hereinbelow.

The aminofunctional siloxane polymer in Comparison Examples 1-8 was a compound having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R is a group having the formula $-CH_2CH_2CH_2-NH-CH_2CH_2-NH_2$. The value of x and y and the acid employed in the particular example are delineated in Table 3 hereinbelow.

Table 3

Comparison Example	x	y	Acid	Wt% Polymer	Wt% Acid	Wt% Water
1	208	4	CH_3COOH	0.0096	0.0003	99.9900
2	208	4	$HOCH_2COOH$	0.0099	0.0052	99.9849
3	208	4	CH_3COOH	0.0097	0.0003	99.9900
4	127	7	CH_3COOH	0.0112	0.0014	99.9874
5	70	8	CH_3COOH	0.0091	0.0009	99.9900
6	70	8	$HOCH_2COOH$	0.0088	0.0064	99.9848
7	70	8	CH_3COOH	0.0091	0.0009	99.9900
8	70	8	$HOCH_2COOH$	0.0091	0.0154	99.9755

The resulting compounds were aminofunctional siloxane polymers having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R is a group having the formula $-CH_2CH_2CH_2-\overset{+}{N}HR^2-CH_2CH_2-\overset{+}{N}H_2R^2 \cdot 2A^-$ where R^2 is a hydrogen atom or a $-CH_2C_6H_5$ group. The value of x and y for the solutions remained the same. The identity of R^2, the identity of A, the mole percent of MeRSiO and the neutralized polymer solubility (weight percent aminofunctional siloxane in H_2O) are delineated in Table 4 hereinbelow. The mole percent of MeRSiO was determined according to the procedure described in Example 1. Comparison Examples 1-8 were all hazy or cloudy and thus determined to be water insoluble.

Table 4

Comparison Example	R^2	A	MeRSiO Mole (%)	Polymer Solubility (wt% in H_2O)
1	-H	CH_3COO^-	2	<0.01
2	-H	$HOCH_2COO^-$	2	<0.01
3	$-CH_2C_6H_5$	Cl^-	2	<0.01
4	-H	CH_3COO^-	5	-
5	-H	CH_3COO^-	8	0.01
6	-H	$HOCH_2COO^-$	8	<0.01
7	$-CH_2C_6H_5$	Cl^-	8	<0.01
8	$-CH_2C_6H_5$	Cl^-	8	<0.01

Examples 11-14

The following compositions of the present invention were prepared by mixing an aminosiloxane solution described below, an acid and water into a container. This mixture was then agitated until the mixture was homogenous. Examples llb, 12b, 13b and 14b and Comparison Examples 9b and 10b were prepared by mixing the aminosiloxane and isopropyl alcohol in a 2000 ml flask. Next, with stirring, benzyl chloride was added with a dropper and the resulting mixture was again stirred. The mixture was then heated to a temperature of 85°C. and then allowed to cool. The amount of aminosiloxane solution or aminofunctional siloxane polymer, acid and water for all the Comparison Examples is delineated

in Table 5 hereinbelow.

Each of the aminosiloxane solutions contained (i) a mixture of an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$, an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, an aminofunctional siloxane having the average formula $HOMe_2SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, (ii) a cyclic aminofunctional siloxane having the average formula

$$\boxed{(Me_2SiO)_{x'}(MeRSiO)_{y'}},$$

and
(iii) a cyclosiloxane having the formula

$$\boxed{(Me_2SiO)_n}$$

where R is a group having the formula $-CH_2CR^1HCH_2-NH-CH_2CH_2-NH_2$ where R^1 is methyl or a hydrogen atom, the value of x'+ y' is from 4 to 9 and n has an average value of 4 to 9. The amount of each component in each solution was as follows: Examples 11a, 11c and 11d contained 79 weight percent of (i), 13 weight percent of (ii) and 8 weight percent of (iii). Example 11b contained 81 weight percent of (i), 11 weight percent of (ii) and 8 weight percent of (iii). Examples 12a, 12c and 12d contained 78 weight percent of (i), 15 weight percent of (ii) and 7 weight percent of (iii). Example 12b contained 77 weight percent of (i), 15 weight percent of (ii) and 8 weight percent of (iii). Examples 13a-13d contained 73 weight percent of (i), 20 weight percent of (ii), 7 weight percent of (iii) and Examples 14a-14d contained 44 weight percent of (i), 51 weight percent of (ii) and 5 weight percent of (iii). The value of x and y, the acid employed in the particular example and the identity of R^1 are delineated in Table 5 hereinbelow.

The aminofunctional siloxanes employed in the comparison examples had the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R is a group having the formula $-CH_2CR^1HCH_2-NH-CH_2CH_2-NH_2$ where R^1 is methyl or a hydrogen atom.

Table 5

Ex.	x	y	R^1	Acid	Wt% Polymer	Wt% Acid	Wt% Water
11a	47	8	-H	CH_3COOH	0.7918	0.2068	99.0014
11b	47	8	-H	CH_3COOH	0.0869	0.0129	99.9002
11c	47	8	-H	$HOCH_2COOH$	0.8079	0.1957	98.9964
11d	47	8	-H	HOC_6H_4COOH	0.6857	0.3136	99.0006
12a	44	9	$-CH_3$	CH_3COOH	2.3971	0.5991	97.0038
12b	44	9	$-CH_3$	CH_3COOH	0.2162	0.0331	99.7508
12c	44	9	$-CH_3$	$HOCH_2COOH$	1.1788	0.3212	98.5000
12d	44	9	$-CH_3$	HOC_6H_4COOH	0.9985	0.4929	98.5086
13a	35	10	-H	CH_3COOH	13.0259	3.2994	83.6747
13b	35	10	-H	CH_3COOH	1.6248	0.3847	97.9905
13c	35	10	-H	$HOCH_2COOH$	13.3802	4.1462	82.4736
13d	35	10	-H	HOC_6H_4COOH	11.7526	7.1993	81.0481
14a	23	13	-H	CH_3COOH	59.0998	20.4340	20.4662
14b	23	13	-H	CH_3COOH	74.1808	15.6196	10.1996
14c	23	13	-H	$HOCH_2COOH$	41.2080	17.3892	41.4028
14d	23	13	-H	HOC_6H_4COOH	42.6109	37.3015	20.0876
Comparison Examples:							
9a	208	4	-H	CH_3COOH	0.0096	0.0003	99.99
9b	208	4	-H	CH_3COOH	0.0097	0.0003	99.99
9c	208	4	-H	$HOCH_2COOH$	0.0099	0.0052	99.9849
9d	208	4	-H	HOC_6H_4COOH	0.0093	0.0008	99.9899

Table 5 (continued)

Comparison Examples							
10a	70	6	-H	CH_3COOH	0.0091	0.0009	99.99
10b	70	6	-H	CH_3COOH	0.0093	0.0007	99.99
10c	70	6	-H	$HOCH_2COOH$	0.0088	0.0064	99.9848
10d	70	6	-H	HOC_6H_4COOH	0.0078	0.0022	99.99

The resulting solutions (examples) contained components (i), (ii) and (iii) in the amounts delineated above however, R was a group having the formula $-CH_2CR^1HCH_2-NHR^2-CH_2CH_2-NH_2R^2 \cdot 2A^-$ where R^1 is methyl or a hydrogen atom and R^2 is a hydrogen atom or a $-CH_2C_6H_5$ group.

The resulting compounds in the comparison examples had the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R is a group having the formula $-CH_2CR^1HCH_2-NHR^2-CH_2CH_2-NH_2R^2 \cdot 2A^-$ where R^1 is methyl or a hydrogen atom and R^2 is a hydrogen atom or a $-CH_2C_6H_5$ group. The value of x, y, x' and y' for the solutions and comparative compounds remained the same. The identity of A, the identity of R^1, the identity of R^2, the mole percent of MeRSiO and the neutralized polymer solubility (weight percent aminofunctional siloxane in H_2O) are delineated in Table 6. The mole percent of MeRSiO was determined according to the procedure of Example 1. Examples 11a-14d were all determined to be water soluble since all of the solutions were clear upon visual inspection.

Table 6

Ex	R^1	R^2	A	MeRSiO Mole (%)	Polymer Solubility (wt% in H_2O)
11a	-H	-H	CH_3COO^-	14	1
11b	-H	$-CH_2C_6H_5$	Cl^-	13	0.1
11c	-H	-H	$HOCH_2COO^-$	14	1
11d	-H	-H	$HOC_6H_4COO^-$	14	1
12a	$-CH_3$	-H	CH_3COO^-	16	3
12b	$-CH_3$	$-CH_2C_6H_5$	Cl^-	16.5	0.25
12c	$-CH_3$	-H	$HOCH_2COO^-$	16	1.5
12d	$-CH_3$	-H	$HOC_6H_4COO^-$	16	1.5
13a	-H	-H	CH_3COO^-	20	16
13b	-H	$-CH_2C_6H_5$	Cl^-	20	2
13c	-H	-H	$HOCH_2COO^-$	20	17.5
13d	-H	-H	$HOC_6H_4COO^-$	20	19
14a	-H	-H	CH_3COO^-	32	80
14b	-H	$-CH_2C_6H_5$	Cl^-	32	90
14c	-H	-H	$HOCH_2COO^-$	32	58.5
14d	-H	-H	$HOC_6H_4COO^-$	32	80
Comparison Examples:					
9a	-H	-H	CH_3COO^-	2	0
9b	-H	$-CH_2C_6H_5$	Cl^-	2	0
9c	-H	-H	$HOCH_2COO^-$	2	0
9d	-H	-H	$HOC_6H_4COO^-$	2	0
10a	-H	-H	CH_3COO^-	8	0
10b	-H	$-CH_2C_6H_5$	Cl^-	8	0
10c	-H	-H	$HOCH_2COO^-$	8	0
10d	-H	-H	$HOC_6H_4COO^-$	8	0

Examples 15-17

The following compositions of the present invention were prepared by mixing an aminosiloxane solution described below, glacial acetic acid and water into a container. This mixture was then agitated until the mixture was homogenous. Comparison Example 11 and 15 were prepared in the same manner as Examples 16 and 17, except that the acid and water were mixed before the water was added.

Each of the aminosiloxane solutions contained (i) a mixture of an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$, an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, an aminofunctional siloxane having the average formula $HOMe_2SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2OH$, (ii) a cyclic aminofunctional siloxane having the average formula

$$\boxed{(Me_2SiO)_{x'}(MeRSiO)_{y'}},$$

and
(iii) a cyclosiloxane having the formula

$$\boxed{(Me_2SiO)_n}$$

where R is a group having the formula where R is a group having the formula $-CH_2CH_2CH_2NH_2$, the value of x'+ y' is from 4 to 9 and n has an average value of 4 to 9. The amount of each component in each solution was as follows: Example 15 contained 85 weight percent of (i), 5 weight percent of (ii) and 10 weight percent of (iii), Example 16 contained 86 weight percent of (i), 8 weight percent of (ii) and 6 weight percent of (iii) and Example 17 contained 77 weight percent of (i), 18 weight percent of (ii) and 5 weight percent of (iii).

The aminofunctional siloxane polymer employed in Comparison Example 11 had the average formula $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R is a group having the formula $-CH_2CH_2CH_2-NH_2$.

The weight percent of siloxane solution, acid and water were as follows:

Table 7

Ex.	x	y	Wt% Siloxane Solution	Wt% Acid	Wt% Water
15	81	23	0.6067	0.0884	99.3049
16	27	16	8.1081	1.8919	90
17	28	40	67.9188	21.5539	10.5273
Compar. Ex.					
11	323	7	0.0098	0.0002	99.99

The resulting solutions (examples) contained components (i), (ii) and (iii) in the amounts delineated above, however, R was a group having the formula $-CH_2CH_2CH_2-NH_3 \cdot CH_3COO^-$

The resulting compound in the comparison example had the average formula: $Me_3SiO(Me_2SiO)_x(MeRSiO)_ySiMe_3$ where R was a group having the formula $-CH_2CH_2CH_2-NH_3 \cdot CH_3COO^-$. The value of x, y, x' and y' for the solutions and comparative compounds remained the same. The mole percent of MeRSiO and the neutralized polymer solubility (weight percent aminofunctional siloxane in H_2O) for the examples and comparison example are delineated in Table 8. The mole percent of MeRSiO was calculated as described in Example 1. Examples 15-17 were both determined to be water soluble since all of the solutions were clear upon visual inspection.

Table 8

Example	MeRSiO Mole (%)	Polymer Solubility (wt% in H_2O)
15	20	0.07
16	32	10.00
17	50	89.50
Compar. Ex.		
11	2	0

Example 18

A composition of the invention was prepared by adding 7.55 (g) of an aminosiloxane solution containing (i) 44 weight percent of a mixture of an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_3$, an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_2OH$ and an aminofunctional siloxane having the average formula $HOMe_2SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_2OH$, (ii) 51 weight percent of an aminofunctional siloxane having the average formula

$$\boxed{(Me_2SiO)_{x'}(MeRSiO)_{y'}} \quad ,$$

and
(iii) 5 weight percent of a cyclosiloxane having the average formula

$$\boxed{(Me_2SiO)_n}$$

where R is a group having the formula $-CH_2C(CH_3)HCH_2-NH-CH_2CH_2-NH_2$, the value of x'+ y' is from 4 to 9 and n has an average value of 4 to 9 and 1.94 (g) of acetic anhydride to a container. The mixture was stirred and then allowed to react. The resulting solution (example) contained components (i), (ii) and (iii) in the amounts delineated above however, R was a group having the formula $-CH_2CH_2CH_2-NH_2-CH_2CH_2-NHR^1 \cdot CH_3COO^-$ where R^1 is $-C(O)CH_3$. The neutralized polymer solubility (weight percent aminofunctional siloxane in H_2O) was 70% by weight in water.

Examples 19-24

A composition of the present invention was prepared by mixing 33 weight percent of an aminosiloxane solution and 3.0 weight percent of glacial acetic acid in a container under nitrogen. Next, 64 weight percent of water was added to this mixture and the mixture was then agitated until it was homogenous.

The aminosiloxane solution contained (i) 44 weight percent of a mixture of an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_3$, an aminofunctional siloxane having the average formula $Me_3SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_2OH$ and an aminofunctional siloxane having the average formula $HOMe_2SiO(Me_2SiO)_{23}(MeRSiO)_{13}SiMe_2OH$, (ii) 51 weight percent of an aminofunctional siloxane having the average formula

$$\boxed{(Me_2SiO)_{x'}(MeRSiO)_{y'}} \quad ,$$

and
(iii) 5 weight percent of a cyclosiloxane having the formula

$$\boxed{(Me_2SiO)_n}$$

where R is a group having the formula $-CH_2CH(CH_3)CH_2-NH-CH_2CH_2-NH_2$, the value of x'+ y' is from 4 to 9 and n has an average value of 4 to 9. The resulting solution (example) contained components (i), (ii) and (iii) in the amounts delineated above however, R was a group having the formula $-CH_2CH(CH_3)CH_2-NH_2-CH_2CH_2-NH_3 \cdot 2CH_3COO^-$. Next, an amount of this solution was mixed with water. The amount of solution and water for each example is shown in Table 9.

Table 9

Example	Wt% Solution	Wt% Water
19	0.1	99.9
20	1.0	99.0
21	5.0	95.0
22	10.0	90.0
23	25.0	75.0
24	50.0	50.0
Blank	0.0	100.0

These examples were then tested for weight percent pick-up, relative hand value, were observed for feel and were observed for the amount of yellowing detected on the fabric the sample was placed on and the results of these tests are delineated in Table 10 hereinbelow. The weight percent pick up is the percent weight gain by the fabric during treatment. For example, if a 5 gram fabric contains 2.5 grams during treatment, the pick up is 50 percent. The relative hand value was determined by a survey of panelists. The panelists first rank treated samples in order of increasing softness. This ranking is then repeated a number of times to insure reproducibility. Samples are then given ratings based on comparisons to the controls and each other. The rating scale is between 1 and 5 in increments of 0.25, with the higher ratings indicating increased softness. A rating difference of 0.25 between samples indicates that the panelists could consistently detect a difference in the softness after handling the samples for a period of 15 seconds. When two samples were 0.50 points apart, panelists could perceive a difference in around 5 seconds, while a difference of 0.75 or higher indicated an immediately noticeable distinction. The amount of yellowing is determined visually and the degree to which the fabric appears to be yellow is recorded. The sample was placed on the fabric by soaking a 12.5 inch by 10 inch 100% cotton sheet in the solution in a 400g bath. The sheet was removed, run through a padder to dry and placed in a 150°C. oven for 3.5 minutes to dry. The sheet was then tested for weight percent pick-up, hand value, feel and yellowing as described above. The results of the test are reported in Table 10 hereinbelow.

Table 10

Example	Wt% Pick-up	Relative Hand Value (5=best)	Feel	Yellowing
19	-2.9*	0.5	Rough	low
20	2.1	1	Rough	low
21	1.6	2	Soft Smooth	low
22	3.2	4	Soft Smooth	yellow
23	7.1	4	Very Smooth Soft	yellow
24	15.5	3	Smooth Rigid	yellow
Blank	0	0	Rough	none

*The sample had a negative pickup due to the heating in the process of padding and curing which caused the untreated fabric to become dehydrated and lose some mass.

It is apparent from Table 10 that the compounds of the present invention render fibers smooth and soft and are thus useful as fiber treatment agents.

Claims

1. A water soluble ammonium siloxane composition comprising:

(A) 0.01 to 90 weight percent of an aminosiloxane blend comprising a mixture of:

(i) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_2SiR_3$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_3$; and

(ii) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$, and

(iii) an aminofunctional siloxane having its formula selected from:

(a) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$;

(B) 0.1 to 90 weight percent of a cyclic aminofunctional siloxane having the average formula:

$$\boxed{(Me_2SiO)_{x'}(RR^1SiO)_{y'}} \quad ,$$

and
(C) 0.1 to 10 weight percent of a compound having the average formula:

$$\boxed{(Me_2SiO)_n}$$

wherein Me denotes methyl, R is independently a monovalent hydrocarbon radical having from 1 to 6 carbon atoms or an aryl radical, R^1 is a group having its formula selected from $-R^3\text{-}NHR^5\text{-}R^4\text{-}NH_2R^5\cdot 2A^-$, $-R^3\text{-}NH_2\text{-}R^4\text{-}NHR^6\cdot A^-$, $-R^3\text{-}NR^6\text{-}R^4\text{-}NH_3\text{-}A^-$, $-R^3\text{-}NH_2R^5.A^-$ and wherein R^3 is a divalent hydrocarbon radical having at least 3 carbon atoms, R^4 is a divalent hydrocarbon radical having at least 2 carbon atoms, R^5 is selected from the group consisting of hydrogen, an alkyl radical having from 1 to 6 carbon atoms, an aryl radical and an arylalkyl radical, R^6 is a $-C(O)R^7$ group where R^7 is selected from a monovalent hydrocarbon group having from 1 to 20 carbon atoms and an aryl radical and A^- is an anion selected from halide anions, carboxylate anions and inorganic oxoanions, R^2 is independently selected from a monovalent hydrocarbon radical having from 2 to 6 carbon atoms and an aryl radical, x has a value of 10 to 10,000, y has a value of 1 to 8,000, z has a value of 1 to 250, x' has an average value of 1 to 8 and y' has an average value of 1 to 8 with the proviso that the value of x'+ y' is from 4 to 9, n has an average value of 4 to 9, with the proviso that the value of y/x+y+z+2 is at least 0.1.

2. A composition according to claim 1 wherein (A)(i) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_3$, (A) (ii) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, (A) (iii) is an aminofunctional siloxane having the formula $HOMe_2SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, and (B) is a cyclic aminofunctional siloxane having the formula:

$$\boxed{(Me_2SiO)_{x'}(MeR^1SiO)_{y'}}$$

wherein R^1 is a group having its formula selected from:

$$-CH_2CH_2CH_2\text{-}\overset{+}{N}H_2\text{-}CH_2CH_2\text{-}\overset{+}{N}H_3\cdot 2A^-,$$

$$-CH_2CH(CH_3)\,CH_2\text{-}\overset{+}{N}H_2\text{-}CH_2CH_2\text{-}\overset{+}{N}H_3\cdot 2A^-,$$

$$-CH_2CH_2CH_2\text{-}\underset{\overset{|}{CH_2C_6H_5}}{\overset{+}{N}H}\text{-}CH_2CH_2\text{-}\underset{\overset{|}{CH_2C_6H_5}}{\overset{+}{N}H_2}\cdot 2A^-,$$

$$-CH_2CH(CH_3)CH_2\text{-}\underset{\overset{|}{CH_2C_6H_5}}{\overset{+}{N}H}\text{-}CH_2CH_2\text{-}\underset{\overset{|}{CH_2C_6H_5}}{\overset{+}{N}H_2}\cdot 2A^-,$$

$$-CH_2CH_2CH_2\text{-}\underset{\overset{|}{C(O)CH_3}}{\overset{+}{N}H_2}\text{-}CH_2CH_2\text{-}NH\cdot A^-,$$

$$-CH_2CH(CH_3)CH_2\text{-}\underset{\overset{|}{C(O)CH_3}}{N}\text{-}CH_2CH_2\text{-}\overset{+}{N}H_3\cdot A^-,$$

and $-CH_2CH_2CH_2\text{-}\overset{+}{N}H_3\cdot 2A^-$, wherein A^- is selected from CH_3COO^-, Cl^-, $HOCH_2COO^-$, $C_6H_5COO^-$ and $HOC_6H_4COO^-$ wherein x, y, x' and y' are as defined above.

3. A method of making a water soluble ammonium siloxane composition comprising mixing:

(I) a solution comprising:

(A) 0.01 to 90 weight percent of an aminosiloxane solution comprising a mixture of:

(i) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR^3$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_3$; and

(ii) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$; and

(iii) an aminofunctional siloxane having its formula selected from:

(a) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$;

(B) 0.1 to 90 weight percent of a cyclic aminofunctional siloxane having the average formula:

$$\overline{\underline{|(Me_2SiO)_{x'}(RR^1SiO)_{y'}|}},$$

and
(C) 0.1 to 10 weight percent of a compound having the average formula:

$$\overline{\underline{|(Me_2SiO)_n|}}$$

wherein Me denotes methyl, R is independently a monovalent hydrocarbon radical having from 1 to 6 carbon atoms or an aryl radical, R^1 is a group having its formula selected from $-R^3NH-R^4-NH_2$ and $-R^3-NH_2$ wherein R^3 is a divalent hydrocarbon radical having at least 3 carbon atoms, R^4 is a divalent hydrocarbon radical having at least 2 carbon atoms, R^2 is independently selected from a monovalent hydrocarbon radical having from 2 to 6 carbon atoms and an aryl radical, x has a value of 10 to 10,000, y has a value of 1 to 8,000, z has a value of 1 to 250, x' has an average value of 1 to 8 and y' has an average value of 1 to 8 with the proviso that the value of x'+ y' is from 4 to 9, n has an average value of 4 to 9 and with the proviso that the value of y/x+y+z+2 is at least 0.1;

(II) an acid compound; and
(III) water.

4. A method according to claim 3 wherein (A)(i) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_3$, (A) (ii) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, (A) (iii) is an aminofunctional siloxane having the formula $HOMe_2SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$ and (B) is a cyclic aminofunctional siloxane having the formula:

$$\overline{\underline{|(Me_2SiO)_{x'}(MeR^1SiO)_{y'}|}}$$

wherein R^1 is a group having its formula selected from $-CH_2CH_2CH_2-NH-CH_2CH_2-NH_2$, $-CH_2CH(CH_3)CH_2-NH-CH_2CH_2-NH_2$ and $-CH_2CH_2CH_2-NH_2$ wherein x, y, x' and y' are as defined above.

5. A method according to claim 3 wherein x has a value of 10 to 100, y has a value of 5 to 50, x' has a value of 2 to 3.5 and y' has a value of 0.5 to 2 with the proviso that the value of x'+ y' is from 4 to 9.

6. A method according to claim 3 wherein the method further comprises adding an acid anhydride during step (I).

7. A method according to claim 3 wherein the method further comprises adding an aryl halide during step (I).

8. A method of treating a substrate, the method comprising the step of:

(I) applying to a substrate a water soluble ammonium siloxane composition wherein the water soluble ammonium siloxane composition comprises:

(A) 0.01 to 90 weight percent of an aminosiloxane solution comprising a mixture of:

(i) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_2SiR_3$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_3$; and

(ii) an aminofunctional siloxane having its formula selected from:

(a) $R_3SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $R_3SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$; and

(iii) an aminofunctional siloxane having its formula selected from:

(a) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_y(RR^2SiO)_zSiR_2OH$ and
(b) $HOR_2SiO(Me_2SiO)_x(RR^1SiO)_ySiR_2OH$;

(B) 0.1 to 90 weight percent of a cyclic aminofunctional siloxane having the average formula:

$$\left[(Me_2SiO)_{x'}(RR^1SiO)_{y'}\right] ,$$

and
(C) 0.1 to 10 weight percent of a compound having the average formula:

$$\left[(Me_2SiO)_n\right]$$

wherein Me denotes methyl, R is independently a monovalent hydrocarbon radical having from 1 to 6 carbon atoms or an aryl radical, R^1 is a group having its formula selected from $-R^3-NHR^5-R^4-NH_2R^5 \cdot 2A^-$, $-R^3-NH_2$ $-R^4-NHR^6 \cdot A^-$, $-R^3-NR^6-R^4-NH_3-A^-$, $-R^3-NH_2R^5 \cdot A^-$ and wherein R^3 is a divalent hydrocarbon radical having at least 3 carbon atoms, R^4 is a divalent hydrocarbon radical having at least 2 carbon atoms, R^5 is selected from the group consisting of hydrogen, an alkyl radical having from 1 to 6 carbon atoms, an aryl radical and an arylalkyl radical, R^6 is a $-C(O)R^7$ group where R^7 is selected from a monovalent hydrocarbon group having from 1 to 20 carbon atoms and an aryl radical and A^- is an anion selected from halide anions, carboxylate anions and inorganic oxoanions, R^2 is independently selected from the group consisting of a monovalent hydrocarbon radical having from 2 to 6 carbon atoms and an aryl radical, x has a value of 10 to 10,000, y has a value of 1 to 8,000, z has a value of 1 to 250, x' has an average value of 1 to 8 and y' has an average value of 1 to 8 with the proviso that the value of x'+ y' is from 4 to 9, n has an average value of 4 to 9 and with the proviso that the value of y/x+y+z+2 is at least 0.1.

9. A method according to claim 8 wherein the method further comprises heating the substrate after step (I).

10. A method according to claim 8 wherein (A) (i) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_3$, (A) (ii) is an aminofunctional siloxane having the formula $Me_3SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$, (A) (iii) is an aminofunctional siloxane having the formula $HOMe_2SiO(Me_2SiO)_x(MeR^1SiO)_ySiMe_2OH$ and (B) is a cyclic aminofunctional siloxane having the formula:

$$\left[(Me_2SiO)_{x'}(MeR^1SiO)_{y'}\right]$$

wherein R^1 is a group having its formula selected from:

$$-CH_2CH_2CH_2-\overset{+}{N}H_2-CH_2CH_2-\overset{+}{N}H_3\cdot 2A^-,$$

$$-CH_2CH(CH_3)CH_2-\overset{+}{N}H_2-CH_2CH_2-\overset{+}{N}H_3\cdot 2A^-,$$

$$-CH_2CH_2CH_2-\underset{\underset{CH_2C_6H_5}{|}}{\overset{+}{N}H}-CH_2CH_2-\underset{\underset{CH_2C_6H_5}{|}}{\overset{+}{N}H_2}\cdot 2A^-,$$

$$-CH_2CH(CH_3)CH_2-\underset{\underset{CH_2C_6H_5}{|}}{\overset{+}{N}H}-CH_2CH_2-\underset{\underset{CH_2C_6H_5}{|}}{\overset{+}{N}H_2}\cdot 2A^-,$$

$$-CH_2CH_2CH_2-\overset{+}{N}H_2-CH_2CH_2-\underset{\underset{C(O)CH_3}{|}}{NH}\cdot A^-,\quad -CH_2CH(CH_3)CH_2-\underset{\underset{C(O)CH_3}{|}}{N}-CH_2CH_2-\overset{+}{N}H_3\cdot A^-$$

and $-CH_2CH_2CH_2-\overset{+}{N}H_3\cdot 2A^-$ wherein A^- is selected from CH_3COO^-, $-Cl^-$, $HOCH_2COO^-$, $C_6H_5COO^-$ and $HOC_6H_4COO^-$ wherein x, y, x' and y' are as defined above.